CALCULATION OF THERMOCHEMICAL CONSTANTS OF PROPELLANTS

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A method for calculation of thermo chemical constants and products of explosion of propellants from the knowledge of molecular formulae and heats of formation of the ingredients is given. A computer programme in Automath-400 has been established for the method. The results of application of the method for a number of propellants are given.

NOTATIONS

a	Number of atoms of carbon
b	Number of atoms of hydrogen
C_v	Specific heat at constant volume (cal/g)
c	Number of atoms of nitrogen
d	Number of atoms of oxygen
E	Internal energy of the gases (cal/g)
F	Force constant of the propellant (J/g)
H_c	Heat of combustion of the propellant (cal/g)
H_f	Heat of formation of the propellant (cal/g)
H_g	Heat of formation of the gases (cal/g)
H_r	Heat of reaction (cal/g)
K_0,	$K_1 \ldots K_6$ Equilibrium constants
M	Molecular weight of the ingredient (g/mole)
m	Mean molecular weight of gases (g/mole)
n	Number of moles of product gases per gramme (mole/g)
p	Pressure of explosion (MPa)
Q	Calorimetric value of propellant (cal/g)
T_0	Temperature of explosoin (°K)
T_a	Approximate temperature of explosion (°K)
t	Initial temperature of propellant (°K)
V	Volume per unit mass of gases (cm^3/g)
v	Gas volume at NTP (cm^3/g)
X	Percentage of the ingredient
η	Co-volume of propellant gases (cm^3/g)
γ	Ratio of specific heats.

The thermochemical constants required to design a propellant for a gun are T_0, F, n, γ, η and the products of explosion (or gas complex). The data needed for computing these are the molecular formulae, heats of formation at constant volume and the percentage of the ingredients. A number of authors have given methods to calculate these parameters.[1, 2] They are satisfactory for approximate calculation, but exact methods are very tedious to handle without a computer[3]. In the present paper the basic principles of calculation[4] are unchanged and a completely new set of equations have been developed for computing the equilibrium constants, mean molecular heats and correction terms for co-volume in the equation of state. The computational procedure has been made suitable for use on a digital computer. The method is applicable for propellants consisting of carbon, hydrogen, nitrogen and oxygen.

METHOD OF CALCULATION

The method of calculation consists of first estimating the approximate temperature of explosion (T_a) and then calculating the products of explosion, the internal energy of the gas complex E and heat of reaction H_r. If T_a is exact temperature of explosion T_0, then we have $E=H_r$. If $E \neq H \simeq, T_a$ is varied suitably and E and H_r are calculated till $E=H_r$.

Let the ith ingredient be $(C_a)_i (H_b)_i (N_c)_i (O_d)_i$. The number of g atom/g of the carbon (C), hydrogen (H) nitrogen (N) and oxygen (O) are given by

$$(C) = 0\cdot01 \; \Sigma \; X_i \, a_i \, / \, M_i$$

$$(H) = 0\cdot01 \; \Sigma \; X_i \, b_i \, / \, M_i$$

$$(N) = 0\cdot01 \; \Sigma \; X_i \, c_i \, / \, M_i$$

$$(O) = 0\cdot01 \; \Sigma \; X_i \, d_i \, / \, M_i$$

$$\eta = C + \tfrac{1}{2} \{(H) + (N)\}$$

$$H_f = 0\cdot01 \; \Sigma \; X_i \, (H_f)_i$$

The energy released at 2500° K (E_{2500}) is given by (assuming that for 77 moles of H_2O there are 23 moles of CO_2)

$$E_{2500} = 52049\,(O) - 38906\,(C) - 6225\,(H) - 6695\,(N) -$$

$$- \left\{ 76550\,(C) - 75050\,(O) + 5000\,(H) + 750\,(N) \right\} \left(\frac{n}{V} \right) +$$

$$+ \left\{ 33\cdot4\,(C) - 1\cdot5\,(H) - 17\cdot0\,(N) - 67\cdot4\,(O) \right\} 10^4 \left(\frac{n}{V} \right)^2 - H_f$$

$$C_v \simeq 1\cdot62\,(C) + 3\cdot265\,(H) + 3\cdot384\,(N) + 5\cdot193\,(O)$$

$$T_a = 2500 + E_{2500} \, / \, C_v$$

The major products of explosion viz. CO_2, CO, H_2O_2, N_2 and H_2 are evaluated

we have

$$\left. \begin{aligned} (N_2) &= \tfrac{1}{2}\,(N) \\ (CO) + (CO_2) &= (C) \\ (H_2) + (H_2O) &= \tfrac{1}{2}\,(H) \\ (CO) + 2\,(CO_2) + (H_2O) &= (O) \end{aligned} \right\} \qquad (1)$$

Water gas reaction is

$$\frac{(CO)\,(H_2\,O)}{(CO_2)\ \ (H_2)} = K_0 \tag{2}$$

$$K_0 = \left[\exp \left\{ -76{\cdot}230 + 18{\cdot}917\, l_n\, T_a - 1{\cdot}1449\, (l_n\, T_a)^2 \right\} \right] \times$$

$$\exp \left[\left\{ 38{\cdot}684 - 0{\cdot}0036646\, T_a + 0{\cdot}43827 \times 10^{-6}\, T_a^{\,2} \right\} \left(\frac{n}{V} \right) + \left\{ 931{\cdot}53 - 0{\cdot}35333\, T_a + 0{\cdot}428 \times 10^{-4}\, T_a^{\,2} \right\} \left(\frac{n}{V} \right)^2 \right] \tag{3}$$

Using equations (1), (2), (3) and putting.

$$l = \{ 0{\cdot}5\,(H) + (C) - (O) \}\, K_0 + (O)$$

$$(CO_2) = \frac{-l \pm \left[l^2 - 4\,(C)\,(K_0 - 1) \left\{ (C) - (O) \right\} \right]^{1/2}}{2\,(K_0 - 1)}$$

only positive value is considered.

The other major products of explosion are computed by

$$(CO) = (C) - (CO_2)$$

$$(H_2O) = (O) - (C) - (CO_2)$$

$$(H_2) = 0{\cdot}5\,(H) - (O) + (C) + (CO_2)$$

$$(N_2) = 0{\cdot}5\,(N)$$

After computing the major products of explosion, the products of dissociation viz (OH), (H_1), (NO), (O_2), (O_1) and (N_1) are calculated (Subscript 1 is added to distinguish the values of atomic composition and atomic states in the gas complex) from the relations

$$(OH) = \frac{(H_2\,O)}{\sqrt{(H_2)}} \sqrt{\frac{V}{82{\cdot}06\, T_a}}\ \exp\left(-\frac{20\, n}{V} \right) K_1$$

$$(H_1) = \sqrt{(H_2)} \sqrt{\frac{V}{82{\cdot}06\, T_a}}\ K_2$$

$$(NO) = \frac{(H_2\,O) \sqrt{(N_2)}}{(H_2)} \sqrt{\frac{V}{82{\cdot}06\, T_a}}\ \exp\left(-\frac{20\, n}{V} \right) K_3$$

$$(O_2) = \left\{ \frac{(H_2\,O)}{(H_2)} \right\}^2 \frac{V}{82{\cdot}06\, T_a} \cdot K_4$$

$$(O_1) = \sqrt{(O_2)} \sqrt{\frac{V}{82{\cdot}06\, T_a}} \cdot K_5$$

$$(N_1) = \sqrt{(N_2)} \sqrt{\frac{V}{82{\cdot}06\, T_a}} \cdot K_6$$

Where the equilibrium constants $K_1, K_2 \ldots\ldots\ldots K_6$ are given by

$$K_1 = \exp\{-547\cdot53 + 126\cdot74\ l_n T_a - 7\cdot3296\ (l_n T_a)^2\}$$
$$K_2 = \exp\{-439\cdot1 + 101\cdot38\ l_n T_a - 5\cdot8382\ (l_n T_a)^2\}$$
$$K_3 = \exp(-164\cdot42 + 19\cdot878\ l_n T_a)$$
$$K_4 = \exp(-241\cdot79 + 29\cdot385\ l_n T_a)$$
$$K_5 = \exp(-120\cdot78 + 14\cdot791\ l_n T_a)$$
$$K_6 = \exp(-176\cdot01 + 21\cdot146\ l_n T_a)$$

These minor products are formed from the major products.

Hence the products are recalculated by reducing (H) by $(OH)+(H_1)$ and (N) by $(NO)+(N_1)$

The value of n, now becomes

$$n = (C) + \tfrac{1}{2}\{(H) + (N)\} + \text{dissociation products.}$$

As stated before we can find CO_2 and the other major products. The dissociation products are recalculated.

The internal energies of these gases are calculated by the equations

$$(E)_{H_2O} = \Big[\Big\{5\cdot1469 + 0\cdot001861\ T_a - 0\cdot1801 \times 10^{-6}\ T_a^2\Big\}\ \delta - \\ - \Big(\frac{n}{V}\Big)\Big\{15240 - 46\cdot352\ T_a + 0\cdot005199\ T_a^2\Big\} + \\ + 35 \times 10^4 \Big(\frac{n}{V}\Big)^2\Big]\ (H_2O)$$

$$(E)_{CO_2} = \Big[\Big\{7\cdot7666 + 0\cdot002032\ T_a - 0\cdot24511 \times 10^{-6}\ T_a^2\Big\}\ \delta - \\ - \Big(\frac{n}{V}\Big)\Big\{134570 - 31\cdot374\ T_a + 0\cdot91663 \times 10^{-3}\ T_a^2\Big\} + \\ + 220 \times 10^4 \Big(\frac{n}{V}\Big)^2\Big]\ (CO_2)$$

$$(E)_{N_2} = \Big[\Big\{4\cdot6373 + 0\cdot8138 \times 10^{-3}\ T_a - 0\cdot9359 \times 10^{-7}\ T_a^2\Big\}\ \delta - \\ - \Big(\frac{n}{V}\Big)\Big\{32172 - 13\cdot603\ T_a + 0\cdot80828 \times 10^{-4}\ T_a^2\Big\} + \\ + 34 \times 10^4 \Big(\frac{n}{V}\Big)^2\Big]\ (N_2)$$

$$(E)_{CO} = \Big[\Big\{4\cdot7314 + 0\cdot80583 \times 10^{-3}\ T_a - 0\cdot9381 \times 10^{-7}\ T_a^2\Big\}\ \delta - \\ - \Big(\frac{n}{V}\Big)\Big\{32172 - 13\cdot603\ T_a + 0\cdot80828 \times 10^{-4}\ T_a^2\Big\} + \\ + 34 \times 10^4 \Big(\frac{n}{V}\Big)^2\Big]\ (CO)$$

$$(E)_{H_2} = \Big[\Big\{4\cdot5344 + 0\cdot51275 \times 10^{-3}\ T_a - 0\cdot26038 \times 10^{-7}\ T_a^2\Big\}\ \delta - \\ - \Big(\frac{n}{V}\Big)\Big\{6297 - 7\cdot0278\ T_a + 0\cdot2034 \times 10^{-3}\ T_a^2\Big\} + \\ + 3 \times 10^4 \Big(\frac{n}{V}\Big)^2\Big]\ (H_2)$$

$$(E)_{O_2} = (5{\cdot}141 + 0{\cdot}72531 \times 10^{-3}\, T_a - 0{\cdot}68137 \times 10^{-7}\, T_a^2)\,(O_2)$$
$$(E)_{OH} = (4{\cdot}5697 + 0{\cdot}58514 \times 10^{-3}\, T_a - 0{\cdot}4102 \times 10^{-7}\, T_a^2)\,(OH)$$
$$(E)_{NO} = (4{\cdot}9632 + 0{\cdot}76776 \times 10^{-3}\, T_a - 0{\cdot}91424 \times 10^{-7}\, T_a^2)\,(NO)$$
$$(E)_{N_1} = 2{\cdot}98\, \delta\, (N_1)$$
$$(E)_{H_1} = 2.98\, \delta\, (H_1)$$
$$(E)_{O_1} = 2{\cdot}98\, \delta\, (O_1)$$

where $\delta = T_a - t$

$$E = (E)_{CO_2} + (E)_{CO} + \ldots\ldots\ldots\ldots + (E)_{O_1}$$
$$H_g = 94020\,(CO_2) + 26700\,(CO) + 57510\,(H_2O) - 5950\,(OH) - $$
$$- 51530\,(H_1) - 81150\,(N_1) - 21500\,(NO) - 58850\,(O_1)$$
$$H_r = H_g - H_f$$

If the initially estimated temperature of explosion T_a is exact then $H_r = E$, if $H_r > E$, T_a is decreased by a small quantity ϵ and if $H_r < E$, T_a is increased by ϵ and the whole calculation is repeated till $H_r = E$. The corresponding temperature is the exact temperature of explosion T_o.

Calculation of Other Constants

Now we can calculate p, η C_v, γ, F, Q, m and v using the equations.

$$p = 8{\cdot}3143 \left(\frac{n}{V}\right) T_o \left(1 + \frac{B_1}{V} + \frac{n}{V^2}\, B_2\right)$$

where B_1 and B_2 are given by

$$B_1 = (18{\cdot}236 - 0{\cdot}0013106\, T_0 + 0{\cdot}96801 \times 10^{-7}\, T_0^2)\,(H_2) +$$
$$+ (29{\cdot}85 + 0{\cdot}0021918\, T_0 - 0{\cdot}4190 \times 10^{-6}\, T_0^2)\,\{ (N_2) + (CO) \} +$$
$$+ (22{\cdot}747 + 0{\cdot}019129\, T_0 - 0{\cdot}26269 \times 10^{-5}\, T_0^2)\,(CO_2) -$$
$$- (27{\cdot}691 - 0{\cdot}01838\, T_0 + 0{\cdot}25601 \times 10^{-5}\, T_0^2)\,(H_2O)$$
$$B_2 = (12{\cdot}461 + 0{\cdot}0054043 T_0 - 0{\cdot}17534 \times 10^{-5}\, T_0^2)\,(H_2) +$$
$$+ (400{\cdot}59 - 0{\cdot}15017\, T_a + 0{\cdot}17977 \times 10^{-4}\, T_0^2)\,\{(N_2) + (CO)\} +$$
$$+ (2610{\cdot}8 - 0{\cdot}97331\, T_0 + 0{\cdot}11544 \times 10^{-3}\, T_0^2)\,(CO_2) +$$
$$+ (425{\cdot}72 - 0{\cdot}16383\, T_0 + 0{\cdot}20169 \times 10^{-4}\, T_0^2)\,(H_2O)$$

$$\eta = V \left\{ 1 - \left(1 + \frac{B_1}{V} + \frac{n}{V^2}\, B_2\right)^{-1} \right\}$$
$$C_v = 12{\cdot}824\,(CO_2) + 6{\cdot}813\,(CO) + 10{\cdot}905\,(H_2O)$$
$$+ 6{\cdot}53\,(H_2) + 6{\cdot}767\,(N_2)$$
$$\gamma = 1{\cdot}0 + \frac{1{\cdot}987\, n}{C_v}$$
$$F = 8{\cdot}3143\, n\, T_0$$
$$Q = 67380\,(O) - 40670\,(C) - H_f$$
$$H_c = 134720\,(C) + 33705\,(H) - 67380\,(O) + Q$$
$$m = 1/n$$
$$v = 22400\, n$$

RESULTS AND CONCLUSION

A computer programme* titled 'THERM' has been established in AUTOMATH-400 language. The programme is extensively used in ERDL for studying the thermochemical properties of conventional as well as new types of experimental formulations. The computed results for a number of conventional propellants

*Available on request from Director, ERDL Pune.

at a loading density of 0·2 g/Cm^3 are given in Tables 1 and 2. The results corroborate the validity of the method proposed in the paper.

TABLE 1

GAS COMPLEX

Propellant	(CO_2) × 10^2	(CO) × 10	(N_2O) × 10	(H_2) × 10^2	(N_2) × 10^2	(O_2) × 10^6	(O_1) × 10^6	(OH) × 10^4	(H_1) × 10^4	(NO) × 10^5	(N_1) × 10^5
	mole/g										
MD	0·3939	0·1750	0·1028	0·5305	0·5021	0·7314	0·9419	0·665	0·9943	0·9705	0·1532
W	0·4337	0·1723	0·0958	0·4415	0·5179	2·061	2·377	0·8504	1·091	1·928	0·2804
WM	0·3962	0·1761	0·1000	0·5166	0·5063	0·7723	0·9965	0·6664	0·9945	1·013	0·1604
SC	0·3340	0·1898	0·0902	0·6025	0·5232	0·1611	2·676	0·4103	0·8337	0·3867	0·0757
HSC	0·6193	0·1337	0·1091	0·2701	0·5391	119·7	74·92	2·436	1·504	25·25	2·224
A	0·1939	0·2271	0·0654	0·9642	0·5043	0·0005	0·0018	0·0711	0·3294	0·0097	0·0035
NH	0·2561	0·2210	0·0687	0·7566	0·4615	0·0010	0·0027	0·0711	0·3013	0·0135	0·0037
N	0·1392	0·1506	0·0736	1·050	1·297	—	0·0003	0·0296	0·1882	0·0045	0·0015
NQ	0·2055	0·1269	0·0968	0·7249	1·304	0·0118	0·0218	0·1863	0·4864	0·1061	0·0211

TABLE 2

THERMOCHEMICAL CONSTANTS

Propellant	T_0 (°K)	F J/g	n (mole/g)	γ	η (Cm^3/g)	E (Cal/g)	Q (Cal/g)
MD	3205 (3220)	1123 (1117)	0·0421 (0·0420)	1·24 (1·24)	0·950 (0·918)	928	1036 (1025)
W	3298 (3300)	1120 (1123)	0·0409 (0·0406)	1·24 (1·24)	0·950 (0·921)	939	1041 (1025)
WM	3212 (3220)	1119 (1117)	0·0419 (0·0417)	1·24 (1·24)	0·950 (0·921)	938	1029 (1013)
SC	3095 (3090)	1098 (1100)	0·0427 (0·0427)	1·25 (1·25)	0·960 (0·936)	877	971 (970)
HSC	3643 (3630)	1184 (1156)	0·0391 (0·0387)	1·23 (1·22)	0·935 (·892)	1076	1200 (1175)
A	2670 (2680)	1019 (1016)	0·0459 (0·0458)	1·26 (1·26)	1·005 (0·968)	735	802 (810)
NH	2680 (2680)	975 (983)	0·0437 (0·0437)	1·26 (1·26)	0·987 (0·957)	718	788 (765)
N	2500 (2430)	983 (983)	0·0473 (0·0472)	1·26 (1·26)	1·000 (1·004)	690	764 (765)
NQ	2846 (2800)	1059 (1061)	0·0447 (0·0447)	1·25 (1·25)	0·958 (0·975)	806	904 (880)

Figures in parenthesis are reported values.

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